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ION BEAM PROCESSING OF DIAMOND

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Ion Beam Processing of Diamond

J.W. Mayer (Cornell) and S.S. Lau (UCSD)

ABSTRACT

The objective of this work was to make an ohmic contact to diamond by the graded band gap concept whereby a smaller band semiconductor is intermixed epitaxially onto a larger band gap material. The project is a joint effort between Cornell University (J.W. Mayer) and the University of California, San Diego (Prof. S.S. Lau) under subcontract to Cornell. The project was successful in that low-resistance contacts to diamond were made by ion beam mixing.

All three aspects of the program were successful:

1. The Cornell group carried out or provided facilities for ion beam deposited at other laboratories.
2. The UCSD group formed ohmic contacts to diamond by depositing Si on Diamond and ion-mixing.
3. The Cornell group demonstrated compound formation between Ni and BP (boron phosphide) which was chosen as a prototype of a high melting point refractory semiconductor with a wide band gap for evaluation of ion beam mixing. JWS

The ohmic contacts to natural type-IIb diamond were formed by depositing Si on the diamond and then ion-mixing the Si with diamond at 700°C with a dose of 2×10^{16} Kr ions/cm². A Si/SiC/diamond structure was formed as evidenced by IR absorption measurements of SiC bands. Contact resistance measurements were made after annealing the ion-mixed sample at 1200°C for 1 hour in flowing forming gas. The specific values determined from

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made after annealing the ion-mixed sample at 1200°C for 1 hour in flowing forming gas. The specific values determined from transmission line measurements were contact resistivity of $6 \times 10^{-4} \pm 3 \times 10^{-4} \Omega\text{-cm}^2$. These values are a factor of two below that of standard, alloyed Au/Ta/diamond contacts.

I. INTRODUCTION

Diamond films are now being formed by a number of research groups. In anticipation of the growth of electronic quality diamond films, J.W. Mayer (Cornell) and S.S. Lau (UCSD) proposed to Max Yoder (ONR) that the Cornell/UCSD groups form ohmic contacts to diamond. The conventional contacts to diamond involve alloying a metal-film, for example Au-Ta, which leads to penetration of alloy spikes into the diamond while the alloyed contacts are adequate for bulk materials, non-uniform, penetrating alloy contacts are unacceptable for diamond-films. Mayer and Lau proposed ion-mixing to form a graded band-gap contact.

The concept of graded-band gaps for ohmic contacts has been used in GaAs structures. The barrier height of metal-Schottky barriers on n-type GaAs is about 0.8 eV and carrier concentrations rarely exceed $5 \times 10^{18}/\text{cm}^3$. Hence tunneling contacts will not be appropriate. However you can grade the band-gap from InAs (easy to contact) on the surface to InGaAs to GaAs. The lattice mismatch of InAs on GaAs is large and grading by way of $\text{In}_x\text{Ga}_{1-x}\text{As}$ is required to prevent internal barriers.

Our proposition for diamond was to make a Si/SiC/Diamond structure. We can make ohmic contacts to silicon. If we could

tailor the structure from Si to $\text{Si}_x \text{C}_{1-x}$ to diamond, we should be able to form a low resistance contact. We chose to use ion-mixing. In this case a layer of Si is deposited on diamond and ion implantation at 700°C (to prevent amorphization) is carried out to intermix the Si and diamond. The concept works.

II. RESULTS

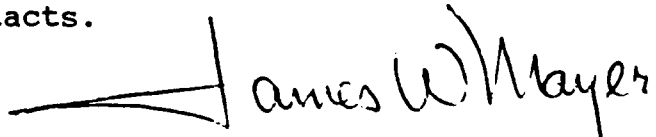
1. The two key papers acknowledging ONR support are included as appendices:

Appendix A. "Ohmic Contacts Formed by Ion Mixing in the Si-Diamond System". F. Fang, C.A. Hewett, M.G. Fernandez and S.S. Lau. IEEE Trans ED 36, 1783 (1989).

Appendix B. "Thermal and Ion Beam Induced Reactions in Ni Thin Films on BP (100)." N. Kobayashi, Y Kumashiro, P. Revesz, Jian Li, and J.W. Mayer. Appl. Phys. Lett. 54, 1914 (1989).

2. Ohmic Contacts to Diamond.

The diamond samples were colorless type IIb p-type diamond with a resistivity of 1200 ohm-cm. A 500 Å Si layer was deposited on the samples, implanted with 2×10^{16} K ions/cm² at 240 keV and annealed at 1200°C for 1 hour in forming gas. The Kr implantation formed an n-type layer on the p-type substrate so that transmission line measurements could be made to evaluate the contacts. The specific contact resistivity is $6 \times 10^{-4} \pm 3 \times 10^{-4}$ $\Omega\text{-cm}^2$. The uniformity and contact resistivity are better than that of conventional Au/Ta diamond contacts.

James W. Mayer

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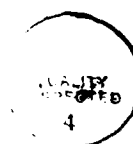
Ohmic Contacts Formed by Ion Mixing in the Si-Diamond System

Fang Fang
Charles A. Hewett
Mark G. Fernandes
S. S. Lau

STATEMENT "A" per Max Yoder
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Ohmic Contacts Formed by Ion Mixing in the Si-Diamond System

FANG FANG, CHARLES A. HEWETT, MARK G. FERNANDES, AND S. S. LAU

Abstract—Graded-bandgap contacts to natural type-IIb diamond were formed by ion-beam mixing of Si (500 Å/diamond samples. Ion mixing carried out using 240-keV Kr⁺ ions at a dose of $2 \times 10^{16}/\text{cm}^2$ at a temperature of 700°C. Si-C bonds were observed by IR absorption measurements, indicating the formation of a Si/SiC/diamond graded structure. Transmission line model (TLM) measurements show that well behaved ohmic contacts can be formed on n-type channels by ion mixing with a subsequent thermal anneal. Samples without ion mixing showed higher specific contact resistivity than ion mixed samples ($\sim 5 \times 10^{-3} \Omega\text{-cm}^2$ versus $\sim 1 \times 10^{-3} \Omega\text{-cm}^2$). For comparison purposes, Au-Ta-based contacts were also prepared.

I. INTRODUCTION

AMONG the group IV semiconductors, diamond is attracting a great deal of interest because of its electrical, physical, and chemical properties. These properties make diamond a leading candidate for high-voltage optoelectronic switching [1], space optics devices [2], and high-temperature devices [3]. In order to fulfill its promise, however, it is necessary to develop an easily fabricated reliable ohmic contact.

Low-resistance ohmic contacts to diamond are difficult to form due to the very wide bandgap of diamond ($E_g = 5.5 \text{ eV}$). A metal deposited on polished n-type diamond will not form a good ohmic contact because of the $\sim 4\text{-eV}$ barrier height [4]. Some limited success has been achieved by mechanically damaging the diamond surface prior to metal deposition, a technique that produces a high surface recombination velocity and inhibits minority-carrier injection. Refractory metals such as tantalum, tungsten, or titanium have also been used on p-type diamond with some success [5], [6]. At high temperatures these metals will chemically react with diamond to form their respective carbides, allowing the alloy to wet the diamond and form a reasonable ohmic contact.

A different approach to forming ohmic contacts was used in this work. We applied the graded-bandgap concept utilized in III-V semiconductor technology to form ohmic contacts. This concept involves the deposition of a smaller bandgap semiconductor onto a larger bandgap

material. A contact is more readily formed on the smaller bandgap material, and current transport across the junction is facilitated by the graded bandgap. This technique was first utilized in the Ge ($E_g = 0.66 \text{ eV}$)/GaAs ($E_g = 1.42 \text{ eV}$) system [7]. We propose the use of two smaller bandgap materials in series to form the graded bandgap to diamond. First, SiC with a bandgap of 2.9 eV (for $\alpha\text{-SiC}$) is utilized to "reduce" the bandgap of diamond from 5.5 eV. Then Si is used to "reduce" the bandgap of SiC to 1.1 eV. Forming an ohmic contact to Si is relatively easy. The graded-bandgap scheme has the further advantage of allowing us to form ohmic contacts to n-type diamond (barrier height $\sim 4 \text{ eV}$). Previous reports have all involved contacts to p-type diamond, with a barrier height of $\sim 1.5 \text{ eV}$. In this work we form the Si/SiC/diamond structure by first depositing Si on diamond. High-temperature ion mixing, plus subsequent thermal annealing, is then used to promote the formation of a uniform SiC layer at the Si-diamond interface. The resulting ohmic contacts are analyzed using a transmission line model (TLM) to determine the contact resistivity. A TLM measurement is the conventionally accepted technique for accurate determination of contact resistivity. The TLM is well documented in the semiconductor technology literature [8]. Briefly, the technique consists of a linear array of equally sized contact pads, with varying contact spacing. Current is passed between two pads, and the voltage drop is measured. The resulting resistance (V/I) is plotted as a function of contact spacing. Extrapolation of the data to zero contact spacing yields the resistance due to the contact itself. In order to correctly apply the TLM technique, one requirement is that current flow between contact pads be two dimensional, i.e., no vertical flow of current in the diamond. Since type-IIb diamond is p-doped, it is necessary to further dope the surface region in order to form a conducting channel. To the best of our knowledge there have been only limited attempts to apply the TLM measurement to diamond, and none of these has utilized a conducting channel. Our n-type channel was formed by high-temperature implantation (concurrent with the formation of the SiC layer).

II. EXPERIMENTAL

Three sample types were prepared. All were natural colorless type-IIb p-type diamonds with a resistivity of $1200 \Omega\text{-cm}$. The sample size was $4 \times 4 \times 0.25 \text{ mm}$. The

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diamonds were etched for 30 min in boiling $\text{HNO}_3:\text{H}_2\text{SO}_4:\text{HClO}_4$ (1:1:1) for the removal of any existing amorphous layer. After cleaning with trichlorethylene, acetone, and isopropyl alcohol, the samples were rinsed in deionized water (18 M Ω) and blown dry with nitrogen.

Sample doping was investigated by implanting Kr^+ into the diamond. The ion energy selected was 80 keV. The dose was systematically varied from $1 \times 10^{15}/\text{cm}^2$ to $5 \times 10^{16}/\text{cm}^2$. After each dose, the diamond was electrically characterized. The process was then repeated for substrate temperatures ranging from room temperature up to 700°C. The implantation current density was held at 1 $\mu\text{A}/\text{cm}^2$ throughout the experiment. The substrate temperature was monitored during implantation with an optical pyrometer focused on the stainless-steel substrate holder.

Ion mixing samples for both metallurgical studies and TLM measurements prepared by e-beam evaporation of a 500-Å Si layer onto a cleaned diamond substrate in a vacuum chamber with a base pressure of 2×10^{-8} torr. The ion energy selected was 240 keV, with a dose of $2 \times 10^{16} \text{ Kr}^+/\text{cm}^2$. The sample was held at 700°C during implant. The energy was sufficient for the Kr ion to penetrate the Si-diamond interface. After implantation the samples were annealed at 1200°C for 1 h in flowing gas (15-percent H_2 , 85-percent N_2). Since not all Si is consumed during ion mixing or thermal annealing, the final structure is Si/SiC/diamond. Infrared absorption analysis of the Si/diamond contacts was used to monitor SiC phase formation.

TLM samples prepared for comparison with ion mixed samples were prepared as follows. First, 150-keV Kr^+ ions were implanted to a dose of $2 \times 10^{16}/\text{cm}^2$ at a temperature of 700°C to form an ~ 500 -Å n-type conducting layer. (TRIM calculations [9] were used for determining the ion energy necessary for creating conducting layers equal in thickness and depth to those created in ion mixing.) Next, a 500-Å Si film was deposited by e-beam evaporation, and the sample was then annealed at 1200°C in flowing forming gas. In addition, in order to compare graded-bandgap contacts to diamond with Au-Ta-based contacts, Au (940 Å)/Ta(100 Å)/diamond contacts were prepared and annealed at 1000°C for 1 h in flowing forming gas.

III. RESULTS AND DISCUSSION

A. Doping of Diamond

Doping of diamonds has been investigated for a number of years with limited success. In-situ doping during growth of both n- and p-type epitaxial layers on synthetic diamond has recently been successful at introducing impurities in an activated state [10]. Ion implantation has also been investigated as a doping technique, primarily by workers in the Soviet Union [11]. Li^+ , B^+ , and P^+ ions have been used with varying degrees of success; however, C^+ and Xe^+ ions may also be used for doping.

TABLE I
CARRIER TYPE FOR DIFFERENT IMPLANT CONDITIONS

Temperature (°C)	Dose (cm^{-2}) (80 keV, Kr^+ ions)					
	1×10^{15}	5×10^{15}	1×10^{16}	2×10^{16}	3.5×10^{16}	5×10^{16}
R.T.	-	p	p	p	p	p
325	-	-	n	n	n	p
450	-	n	n	n	n	n
600	n	n	n	n	n	n
700	n	n	n	n	n	n

suggesting that radiation damage may be responsible for the observed change in conductivity [10], [12]. Experiments have shown that the conductivity is dependent on the ion dose, dose rate, and the temperature during implantation [12]. For this study we are interested in ion mixing of Si on diamond, necessitating the use of a "heavy" ion. Kr^+ ions were chosen as having the most suitable mass-ion range combination. Four-point probe measurements were used to determine sheet resistance after implantation. Additionally, hot probe measurements were carried out to determine carrier type. The results are summarized in Table I and Fig. 1. Room-temperature implantation resulted in p-type conductivity, possibly indicating the formation of a graphitic layer. Higher temperature during implantation gives n-type conductivity up to much higher doses. Subsequently post-implant annealing of these n-type layers at 1200°C resulted in a slight increase in sheet resistance, but the layer remained n-type. Because ion mixing is more efficient at high temperature, the remainder of this investigation was carried out with implantations at 700°C.

B. SiC Formation

Infrared absorption analysis for wavelengths between 2 and 25 μm was used to monitor the formation of SiC and subsequent structural changes after ion mixing and thermal annealing. SiC has an intense absorption band at 797 cm^{-1} due to photon interaction with transverse optical phonons (Si-C bonds) [13]. Fig. 2 shows the absorption spectra obtained in the as-deposited sample (dotted line), after 1-h anneal in flowing forming gas at 1200°C (dashed line), and after ion mixing with $2.1 \times 10^{16} \text{ Kr}^+/\text{cm}^2$ at an energy of 240 keV and substrate temperature of 700°C plus a 1200°C anneal in flowing forming gas (solid line). After annealing, an absorption band near 797 cm^{-1} appears. The peak height increases after Kr^+ ion mixing and a high-temperature anneal. This is taken as an indication that ion mixing leads to the enhancement of the SiC structure. Diamond is relatively inert even at temperatures as high as 1200°C; the ion mixing may thus help to break carbon-carbon bonds. (Diamond has a vacancy formation energy of 3.7 eV versus 2.1 eV for Si and 1.9 eV for Ge.)

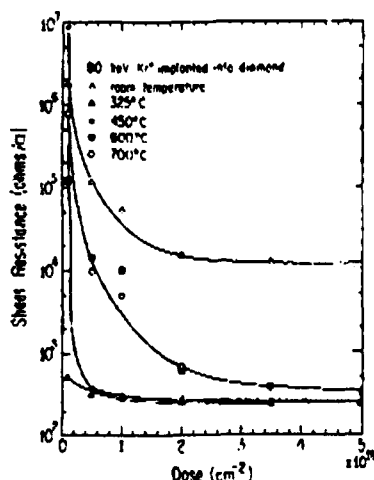


Fig. 1. Sheet resistance versus dose for diamond samples sequentially implanted with 80-keV Kr^+ at various temperatures. Dose rate was held at $1 \mu\text{A}/\text{cm}^2$.

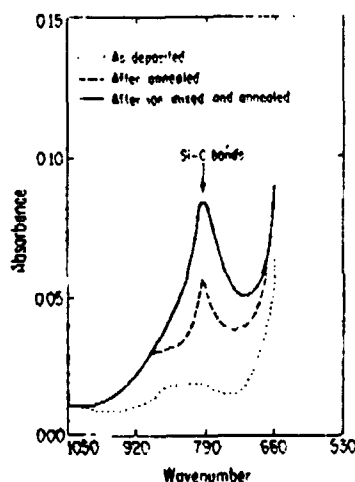


Fig. 2. The IR absorption spectra of Si/diamond samples annealed at 1200°C , for 1 h in flowing forming gas with and without ion mixing.

C. Formation of Ohmic Contacts

A metal-semiconductor ohmic contact is formed by lowering the effective barrier height or by doping the semiconductor very heavily in the vicinity of the contact. In the high doping case, although the barrier height remains the same, the barrier thickness is greatly reduced, and charge carriers in the semiconductor can easily tunnel through the barrier.

It is difficult to form ohmic contacts on wide-bandgap materials such as diamond for two reasons. First, diamond (a covalent semiconductor) has a barrier height essentially independent of the metal work function [4]. Second, it is difficult to produce a heavily doped surface layer in diamond structure. In this work, the graded-bandgap contacts to diamond involve the Si/SiC structure.

Specific contact resistivity was determined using TLM measurements. To the best of our knowledge this is the first time TLM measurements have been carried out using

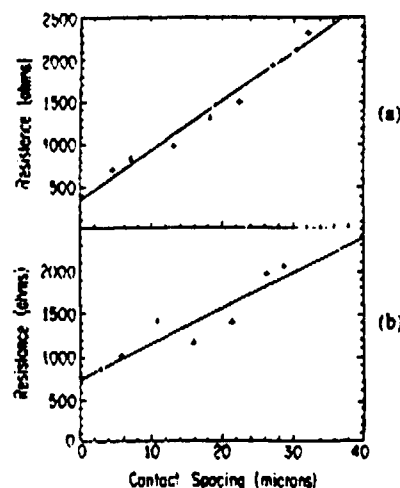


Fig. 3. (a) Measured contact resistance as a function of contact spacing for the ion mixed Si/diamond sample after annealing at 1200°C for 1 h in flowing forming gas. The specific contact resistivity calculated from this data is $6.68 \pm 3.78 \times 10^{-4} \Omega\text{-cm}^2$ with a linear correlation coefficient of 0.98. (b) Measured contact resistance as a function of contact spacing for the Si/diamond sample after annealing at 1200°C for 1 h in flowing forming gas. The specific contact resistivity calculated from this data is $4.78 \pm 2.15 \times 10^{-3} \Omega\text{-cm}^2$ with a linear correlation coefficient of 0.92.

an n-channel region in diamond. Since the bulk diamond is p-type, this avoids bulk conduction and gives an accurate TLM measurement. Contact pads ($150 \mu\text{m}$ square) with varying intercontact spacing (2 to $32 \mu\text{m}$) were formed on diamond (500 \AA , n-type, $2 \times 10^{16}/\text{cm}^2$ Kr^+ implanted) substrates. Test structures were isolated by CF_4 plasma etching at a power of 100 W to form mesa structures. The injected current for the TLM measurement is 1 mA. The best measured contact resistances of the Si/diamond contacts with and without ion mixing as a function of contact spacing are shown in Fig. 3(a) and (b), respectively. The linear correlation coefficient is 0.98 in the case of the ion mixed contacts, and 0.92 in the case of the non-mixed contacts. The actual specific contact resistivities are $6 \times 10^{-4} \pm 3 \times 10^{-4} \Omega\text{-cm}^2$ and $4.78 \times 10^{-3} \pm 2.15 \times 10^{-3} \Omega\text{-cm}^2$ for the ion mixed and non-mixed contacts, respectively. It is clear, then, that the ion mixed sample has a lower contact resistivity and better linear correlation. This may be taken as an indication of the usefulness of ion mixing in the formation of more Si-C bonds, a necessity for the formation of a well behaved graded-bandgap ohmic contact. A summary of experimental results is presented in Table II. The average specific contact resistivity of Au/Ta/diamond contacts is comparable with that of ion mixed Si/diamond contacts. However, the standard deviation in contact resistivity for the Si/diamond contacts is half that of Au/Ta/diamond contacts. Au/Ta/diamond alloyed contacts may have metallic penetration into the diamond, as evidenced by the substantial roughness observed on the contact surface. This could lead to contact spiking or difficulties in producing the planar device structures favored in integrated circuit fabrication.

TABLE II
OHMIC CONTACTS TO DIAMOND

Sample Type	Contact System	Thickness (\AA)	Treatment	Specific Contact Resistivity ($\Omega\text{-cm}$) ^(a)	Comments
1	Si/diamond	500	ion mixed and annealed at 1000 or 1200°C, 1 hour	$\sim 1 \times 10^{-3}$	uniform contact
2	Si/diamond	500	annealed at 1000 or 1200°C, 1 hour	$\sim 5 \times 10^{-3}$	uniform contact
3	Au/Ta/diamond	940/100	annealed at 1000°C, 1 hour	$\sim 1 \times 10^{-3}$	non-uniform alloyed contact

(a) Average value for each sample type.

(b) Although type 1 and type 3 contacts have a similar mean value, the distribution of measured values is much more closely spaced for the Si/diamond (type 1) contacts.

IV. SUMMARY

Kr⁺ implantation into diamond with different doses and sample temperatures was investigated. It was found that the surface layer of the diamond could be made n-type with a five to six orders of magnitude decrease in sheet resistance. IR absorption measurements show that annealing of Si on diamond at 1200°C leads to the formation of SiC. High-temperature ion mixing prior to annealing enhances the formation of SiC. TLM measurements showed that well behaved ohmic contacts on n-type diamond can be formed with a graded-bandgap Si/SiC/diamond structure formed by ion mixing. The uniformity of such contacts is much better than that of conventional Au/Ta/diamond contacts. Au/Ta/diamond alloyed contacts may have metallic penetration into the diamond.

ACKNOWLEDGMENT

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Thermal and ion beam induced reactions in Ni thin films on BP(100)

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Thermal and ion beam induced reactions in Ni thin films on BP(100) have been investigated. For thermally annealed samples the reaction of the Ni layer on BP started at temperatures between 350 and 400 °C and the formation of the crystalline phase corresponding to a composition of Ni_4BP was observed at 450 °C. It was observed that oxygen in the Ni layer could retard the progress of the reaction. The full reaction of the Ni layer with BP induced by energetic heavy ion bombardments (600 keV Xe) was observed at 230 °C. The crystalline phase has the same composition and x-ray diffraction pattern for both thermal and ion-induced reactions.

BP (boron phosphide) is one of the attractive electronic materials as a refractory semiconductor with a wide band gap of 2.1 eV. This compound is also characterized by several outstanding properties such as a high melting point above 3000 °C, a high decomposition temperature of about 1130 °C under 1 atm, extreme hardness, and high oxidation resistance at high temperatures. The fabrication of the Schottky barrier diodes using BP wafers has been reported.¹ Recently, attention has been focused on the ion beam induced epitaxial crystallization (IBIEC) in BP.²

The investigation of the mechanism of the reaction of metals with BP attracts interest from the technological view of the device applications of BP and also physical and chemical views of the reaction of metal thin films on the refractory compound semiconductor. Ion-induced reactions in thin-film systems, on the other hand, have been used to form many phases from equilibrium to amorphous phase and can provide a knowledge of production of innovative materials.³ From these points of view, this research work was intended to make an investigation on the fundamental mechanism of reactions of the metal BP system. In this letter we present the first observation of both thermal and ion beam induced reactions of Ni thin films on BP(100). The striking result is that the reaction temperature was around one-fifth of the melting point (K).

Wafers with BP film thicknesses of around 1 μm were prepared by the thermal decomposition of B_2H_6 and PH_3 in a hydrogen atmosphere on Si(100) substrates at temperatures between 950 and 1150 °C.⁴ All wafers were confirmed to be grown epitaxially by reflective high-energy electron diffraction (RHEED) and channeling experiments using MeV He ions. Ni thin layers with a thickness between 50 and 150 nm were deposited onto BP(100) wafers at room temperature (RT) by evaporation with the resistive method and with the electron beam (EB) method. The pressure during evaporation was 4×10^{-5} Torr for the resistive method and was less than 4×10^{-7} Torr for the EB method. For the thermally induced reaction experiments, samples were annealed in the vacuum (1.5×10^{-7} Torr) at a given temperature for 30 min. In order to investigate the ion beam induced reactions, samples with the thickness of 50 nm of the Ni layer

were bombarded with 600 keV Xe^{2+} ions. The projected range and the straggling of 600 keV Xe ions in Ni are 71.4 and 12.7 nm, respectively.

Analyses of the thickness, compound composition, and homogeneity of the reacted layers of Ni with BP were performed with the Rutherford backscattering (RBS) measurements using a 2 MeV He^{2+} ion beam. Observations with x-ray diffraction were also performed in order to investigate the phase of the reacted layer. Auger electron spectrometry (AES) was employed for the depth analysis of the composition in the layers.

For the samples deposited in a poor vacuum with the resistive method (sample I), the reaction of the Ni layer started at 350 °C and proceeded up to the formation of the reacted layer with 100 nm thickness at 400 °C. Although the Ni layer was only partly consumed, the reaction proceeded no further up to 500 °C. Figure 1 shows the RBS spectrum of this partly reacted Ni layer on BP after annealing at 450 °C. For the samples deposited in the clean vacuum with the EB

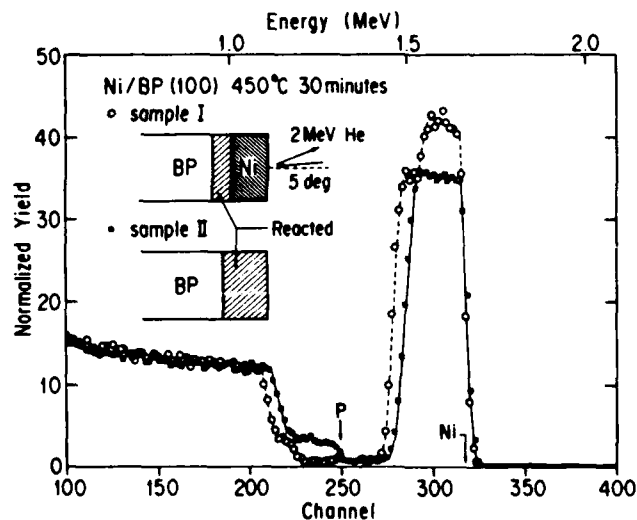


FIG. 1. RBS spectra of partly reacted Ni layer on BP(100) [sample I (contaminated)] and fully reacted layer [sample II(clean)] with 2 MeV He ions after the thermal annealing at 450 °C.

method (sample II), the reaction started at 400 °C. Thermal annealing at 450 °C has induced the fully reacted layer of Ni with BP. The RBS spectrum of this sample is also shown in Fig. 1 after the annealing. The compound composition of the reacted layer determined by the RBS measurements has the atomic ratio for Ni:B:P to be 4:1:1 both in samples I and II.

The depth profile of the composition of the partly reacted layer (sample I) observed with the AES measurements is shown in Fig. 2. The composition of the reacted layer derived from the AES analysis has coincided with that derived from the RBS analysis. One can observe oxygen atom accumulation at the interface between the Ni layer and the reacted layer. This suggests that oxygen atoms have an important role in the retardation of the progress in the reaction in the Ni layer on BP.

Ion bombardment experiments were performed for the samples with a thin clean Ni layer deposited with the EB method (sample III). Figure 3 shows the RBS spectra of the sample before and after the ion bombardment with 600 keV Xe^{2+} ions. One can see the fully reacted layer of Ni on BP after the ion bombardment at 230 °C with the fluence of 5×10^{15} ions/cm² together with the spectrum of the sample before bombardment. The reacted layer has the same composition ratio as that of the thermally reacted layer from the analysis of the RBS measurements.

Thin-film x-ray diffraction experiments on the fully reacted layer (sample II) have revealed that this layer has a crystalline phase. The ion-induced layer (sample III) has also shown the same diffraction pattern. As an example of the reaction of metal films on a refractory compound semiconductor, the reaction of Ni on SiC was reported.⁵ In this case, the first phase is thought to be a binary phase (Ni_3Si_2) and no reaction of Ni with C atoms was observed. In contrast to the case of SiC, a ternary phase (Ni_4BP) or mixed binary phase ($\text{NiB} + \text{Ni}_3\text{P}$) is thought to be the can-

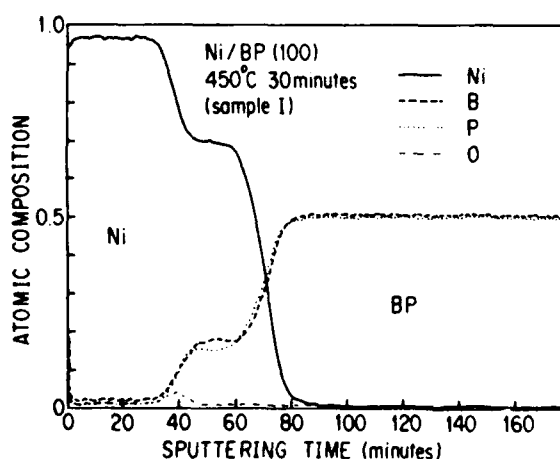


FIG. 2. Depth profile of the composition observed in the partly reacted Ni layer on BP(100) (sample I) after the thermal annealing at 450 °C by the AES measurements.

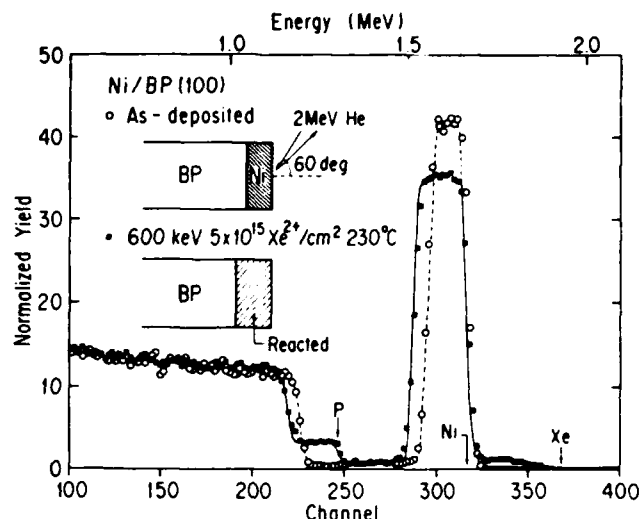


FIG. 3. RBS spectra of Ni on BP(100) (sample III) before and after the 600 keV Xe^{2+} bombardments with the fluence of 5×10^{15} ions/cm² at 230 °C.

didate for the reacted phase of Ni thin film on BP from the x-ray diffraction experiments. The dominant moving species in the reaction of Ni on BP is thought to be Ni from the results of the oxygen accumulation between the reacted layer and the nonreacted layer.⁶

In conclusion, we have observed the reaction of Ni thin films on BP(100) at temperatures around 400 °C for the thermal reaction and around 200 °C for the ion beam induced reaction. Metal-rich ternary phase or mixed binary phase is thought to be the first crystalline phase formed both in the thermal and ion beam induced reactions. Although further studies on kinetics of the compound growth are necessary for the detailed investigation of the reaction mechanism, it is noted that the reaction of Ni thin films on refractory BP was found to occur at temperatures as low as one-fifth of the melting point (K).

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